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Measurements of Polycyclic Aromatic Compounds in the Cylinder of an Operating Diesel Engine

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by

David B. Kittelson and Cao-Jian Du
University of Minnesota
Minneapolis, MN

and

Roy B. Zweidinger
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC27711

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Measurements of Polycyclic Aromatic Compounds in the Cylinder of an Operating Diesel Engine

Cao-Jian Du
Department of Mechanical Engineering,
University of Minnesota
(On leave from the Department
of Research and Development,
Shanghai Diesel Engine Works,
Shanghai, People's Republic of China)

David B. Kittelson
Department of Mechanical Engineering,
University of Minnesota

Roy B. Zweidinger
U.S. Environmental Protection Agency,
Research Triangle Park, NC

ABSTRACT

A unique system which allows sampling of the entire contents of one of the cylinders of a 5.7-liter V-8 indirect-injection diesel engine has been developed. An explosively actuated cutter ruptures a diaphragm in the combustion chamber and allows the contents of the cylinder to rush out and be subsequently diluted and quenched with cool nitrogen. Particles are collected with a high-volume impactor/filter system. This system has been used to collect a series of particle samples at crankangles ranging from 5 to 40 degrees after top dead center. Particle samples from the exhaust were also obtained. The samples have been extracted to determine the soluble organic fraction. These extracts have been analyzed for five polycyclic aromatic compounds: pyrene, fluoranthene, benz(a)pyrene, benz(k)fluoranthene, and 1-nitropyrene. The results indicate significant removal of the first four between the combustion chamber and the exhaust manifold. The 1-nitropyrene behaves differently, however, with higher concentrations in the exhaust samples than in the cylinder samples. This suggests that 1-nitropyrene is formed during the expansion stroke and/or in the exhaust manifold.

MUCH OF THE CONCERN about potential environmental hazards associated with diesel engines has resulted from the identification of potentially mutagenic and/or carcinogenic compounds in diesel exhaust particulate matter. Compounds of concern include many polycyclic aromatic compounds (PACs), i.e., polycyclic aromatic hydrocarbons (PAHs) and their derivatives (1-5*). A number of recent studies have focused on nitrated polycyclic aromatic hydrocarbons and have suggested that they are a principal source of the observed mutagenic activity of diesel exhaust particle extracts (6-7). There is considerable uncertainty about how such compounds are formed and, in fact, there is some doubt about whether they are truly present on diesel exhaust particles as emitted or are formed during sampling (6,8,9).

In order to shed further light on such questions, a series of experiments have been performed in which the concentrations of several PACs have been determined in the combustion chamber and in the exhaust of a single-cylinder version of a passenger-car diesel engine. Five compounds were monitored: 1-nitropyrene, pyrene, benz(a)pyrene (B(a)P), benz(k)fluoranthene (B(k)F), and fluoranthene.

EXPERIMENTAL APPARATUS

The heart of the experimental apparatus is a unique single-cylinder version of a 1979 5.7-liter Oldsmobile V-8 diesel engine. This engine is equipped with a sampling system which is capable of removing, quenching, and diluting essentially the entire contents of the cylinder during actual engine combustion. The system has been described in detail in several previous publications (10-12). Figure 1 shows the general arrangement of the single-cylinder engine and sampling

*Numbers in parentheses refer to references at the end of the paper.

system. The cylinder contents are dumped at a predetermined point in the engine cycle by cutting a 14-mm diameter diaphragm which is mounted flush with the surface of the prechamber. The characteristic time for blowdown and primary quenching is about 0.5 ms. Samples undergo an essentially adiabatic expansion into the sampling apparatus, where they are diluted with nitrogen in a ratio of about 10 to 1. The diluted combustion-chamber contents then flow into a polyethylene sampling bag which has been filled with enough nitrogen to give an overall dilution ratio of approximately 330 to 1. The initial temperature of both the primary and secondary (bag) dilution nitrogen is ambient (300 K).

This dilution process is intended to minimize chemical reactions during sampling. For the engine condition examined in this study, the temperature of the diluted sample was only slightly, never more than 5 K, above ambient. Reactive species were present in very low concentrations, e.g., NO_x and NO_2 were always less than 0.23 and 0.07 ppm, respectively.

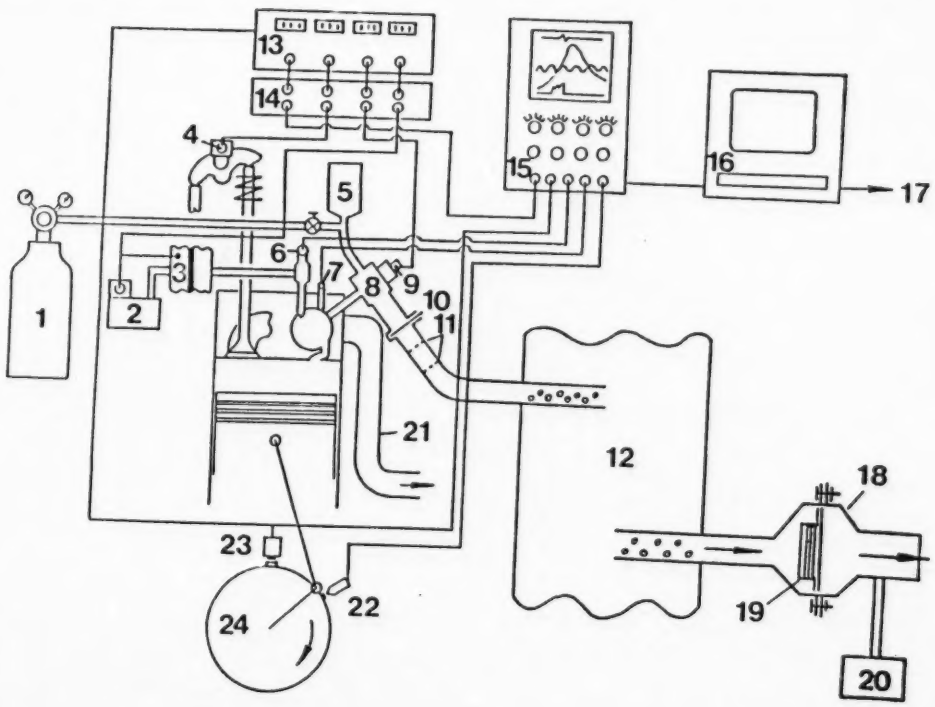

Figure 1 - Schematic of the engine, dumping system, sampling system, dilution system, and measurement system. Components corresponding to numbers on figure

1. nitrogen cylinder; 2. fuel injection pump; 3. magnetic fuel-line break device; 4. magnetic valve deactuator; 5. dilution nitrogen bottle; 6. injector needle-lift pickup; 7. combustion-chamber pressure transducer; 8. prechamber dumping apparatus; 9. squib; 10. sampling valve; 11. shock-wave silencer; 12. sampling bag; 13. four-channel, phase-locked loop electronic timer; 14. four-channel high-current driver; 15. digital oscilloscope; 16. computer terminal; 17. computer center; 18. high-volume slotted cascade impactor; 19. filter; 20. constant-flow controller; 21. exhaust pipe; 22. crankangle marker pickup; 23. magnetic TDC pickup; 24. flywheel of the engine

The influences of gas-phase reactions are further reduced and wall interactions in the sampling bag are minimized by removing the sample from the bag as quickly as possible. This is done using a high-volume sampler equipped with a four-stage slotted impactor. The flow through this system is held constant at 800 liters per minute (Lpm), which is sufficient to empty the bag completely in 10 to 15 s. The impactor stages have cut sizes of 7.7, 3.6, 1.5, and 1.2 μm aerodynamic diameter. In order to minimize particle bounce, impactor substrates consisting of Pallflex TX40HI20-WW filters coated with silicon grease were used (13). All particles smaller than 1.2 μm aerodynamic diameter are collected by a 8 x 10 in. Pallflex TX40HI20-WW back-up filter.

Exhaust samples were collected using the system shown in Figure 2. A portion of the exhaust flows through a short transfer line, through a flow-metering orifice, to a mini-dilution tunnel. The transfer line is heated, and the orifice has been designed to minimize particle loss. The same high-volume impactor filter system that is used in the total cylinder sampling experiments is also used to collect particles from the mini-dilution tunnel. This system also provides the flow of dilution air through the mini-dilution tunnel. A sample flow-rate of 3.7 Lpm is used in conjunction with a mini-tunnel flowrate of 800 Lpm to give an overall dilution ratio of approximately 220 to 1. The dilution ratio was determined by measuring the concentrations of NO_x in the exhaust and in the dilution tunnel. This technique was verified under several conditions using CO_2 as a tracer instead of NO_x.

This high dilution ratio kept the filter temperature less than 1 K above ambient and kept NO_x and NO_2 concentrations below 0.34 and 0.10 ppm, respectively.

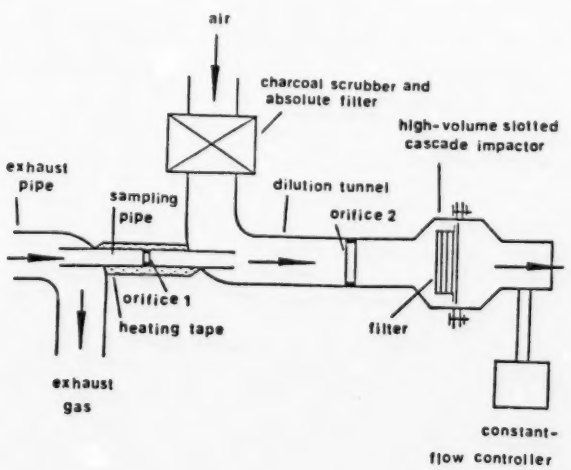

Figure 2 - Schematic of the exhaust particle sampling system

PROCEDURE

The engine specifications and operating conditions are indicated in Table 1. A standard Phillips diesel

Table 1 - Engine Specifications and Operating Conditions

Engine Specifications		
Bore (mm)		103.0
Stroke (mm)		86.3
Displacement (L)		0.714
Strokes/Cycle		4.0
Compression Ratio		22.5:1
Main-Chamber Clearance Volume (L)		0.0194
Prechamber Volume (L)		0.0140
Injection Pump	Roosa-Master Model DB2 distributor pump	
Nozzle	Fixed orifice type with two 0.04318 cm diameter holes	
Intake Valve	opens	6°BTC
	closes	38°ABC
Exhaust Valve	opens	64°BBC
	closes	17°ATC
Engine Operating Conditions		
Engine Speed		1000 r/min
Equivalence Ratio		0.32
Dynamic Injection Timing		3.5 CAD BTDC
Oil Temperature		85 - 90°C
Coolant Temperature		85 - 90°C
Exhaust Temperature		170 - 180°C
NO_x		68 - 75 ppm
Bosch Smoke Number		1.0 - 1.1

Table 2 - Fuel Properties (from Phillips Chemical Company)

DIESEL CONTROL FUEL D-2

LOT C-747

Test	Results	Specifications	ASTM Method
Distillation Range			
IBP, °F	386	340 - 400	D86
10 Percent Point, °F	430	400 - 460	
50 Percent Point, °F	506	470 - 540	
90 Percent Point, °F	576	550 - 610	
EP, °F	610	580 - 660	
API Gravity, 60 F	35.8	33 - 37	D287
Total Sulfur, Weight %	0.20	0.2 - 1.5	D3120
Hydrocarbon Composition, LV%, Aromatics	29.1	33 desired ± 2	D1319
Flash Point, °F	157.0	130 min.	D93
Viscosity, cSt	2.5	2.0 - 3.2	D445
Particulate Matter, mg/L	2.389		D2276
Cetane Number	47.5	42 - 50	D613

control fuel was used. Its properties are listed in Table 2. The engine was lubricated with Mobil Delvac I synthetic lubricant. This oil had a very low vapor pressure, which should prevent significant carry-over of oil vapor onto the particles during the total cylinder sampling experiments. The engine was loaded with a DC dynamometer. Air flow was measured with a laminar flow element, and fuel flow with a burrette. Cylinder pressure was measured using a quartz pressure transducer in the prechamber and fuel injection timing was measured with a needle-lift sensor. Pressure and needle-lift data for each blowdown experiment were recorded with a digital oscilloscope. The cylinder pressure data were used to determine the timing of the blowdown process.

Prior to each blowdown experiment, the engine was carefully cleaned using the cleaning procedures described by Du and Kittelson (12). The engine was then brought up to normal operating temperature using preheating systems on both the lube oil and coolant. The engine was motored to the desired speed, in the case of these experiments, 1000 rpm, and then allowed to stabilize. Next, the fuel was turned on and the engine was allowed to fire for approximately 20 seconds, which is the time required for the fuel injection system and the combustion chamber to approach steady-state conditions. Finally, the blowdown experiment was performed. Two types of blowdown experiments, fired and non-fired, were done. In a fired experiment, the cylinder sample was obtained on a normal fired cycle. In a non-fired experiment, everything was done in exactly the same way, except that no fuel was injected on the blowdown cycle.

It was necessary to do both fired and non-fired experiments because the dumping process is so vigorous that significant quantities of particulate matter are blown from the walls of the combustion chamber by the sampling process itself. Thus, a blowdown sample contains two components: particles produced during the engine cycle in question and particles produced in previous cycles. Most of the material from previous cycles results from reentrainment from the combustion chamber walls by the blowdown process. The net particle concentration produced on a given cycle is taken to be the difference between the particle concentration produced on a fired cycle and the particle concentration produced on a non-fired cycle at the same crankangle position.

Figure 3 shows typical pressure-versus-crankangle profiles observed during normal engine combustion and during a typical blowdown experiment. The sampling process is not instantaneous. Consequently, it is necessary to define some point on the pressure decay curve which is taken as the characteristic crankangle of blowdown. Our usual procedure is to use the 50% pressure decay angle, θ_{hd}, the crankangle at which the cylinder pressure has fallen to half of its value at the beginning of blowdown. In all of the subsequent discussions, this definition will be used.

A single blowdown experiment usually produces around 1.5 mg of particulate matter. This is insufficient for chemical analysis. Consequently, several consecutive blowdown experiments were done at each value of θ_{hd}. The samples were combined by using the same filter and impactor substrate sets for a series of experiments at a given value of θ_{hd}. For most of the conditions examined here, six blowdowns were performed at each sampling angle.

The exhaust samples were obtained with the engine operating steadily at the same speed and load conditions as for the total cylinder samples. Sampling times were 20 and 66 minutes.

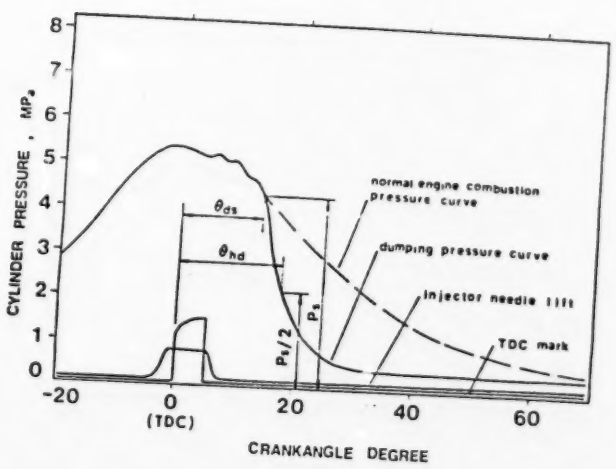

Figure 3 - Cylinder pressure traces for normal operating cycle and blowdown cycle

CHEMICAL ANALYSIS

The filters were soxhlet extracted overnight with dichloremethane and the extracts filtered through a 0.2 µm Fluoropore filter. After concentration by rotary evaporation, the extracts were transferred to tared vials and evaporated to dryness under nitrogen at room temperature. Extract samples were redissolved in 1 mL of dichloromethane for analysis of 1-nitropyrene using the method of Tejada, et al. (14). Pyrene, benz(a)pyrene, benz(k)fluoranthene and fluoranthene were analyzed by reverse phase HPLC using fluorescence detection. The lubricating oil and fuel were also analyzed by diluting 1:60 in hexane-dichloromethane.

RESULTS AND DISCUSSION

Table 3 summarizes the physical measurements made in these experiments. Particles were collected at crankangle positions ranging from 8 to 33 degrees ATDC for fired blowdowns and from 7 to 40 degrees ATDC for non-fired blowdowns. Two exhaust samples were also obtained. In addition, three blank filters were extracted to determine the amount of background extractable material present in the filter media. This material did not contain measurable concentrations of PACs. The extractable masses given are the difference between measured mass and the average filter blank. Particle mass concentrations given below are for particles smaller than 1.2 µm aerodynamic diameter, i.e., the particles collected on the back-up filters. This constituted about 60 % of the total mass collected in the blowdown experiments and about 85 % of the total mass collected in the exhaust sampling experiments. Only the sub-1.2 µm particles were considered because this size range is least influenced by particle reentrainment during sampling. Furthermore, larger particles have been shown to contain low concentrations of PAHs (15) and are therefore of little interest in this study.

The variation sub-1.2 µm particle mass concentration in the cylinder (referred to standard pressure and temperature) with θ_{hd} is plotted in Figure 4. The results for fired, non-fired, and exhaust samples are shown. The fired samples give significantly higher concentrations than the non-fired samples. The concentration of

Table 3 - Particle-Mass and Extractable-Mass Concentrations

Sample	Total Sampling Time (Min)	CAD[a]	Filter Load[b] (mg)	Net Extract[c] (mg)	% Extract	Particle Mass Concentration ($g\ m^{-3}$)	Extractable Mass Concentration ($g\ m^{-3}$)
				Fired Samples			
B	1.5	8	8.8	1.72	19.5	2.6	0.51
E	1.5	13	8.6	0.99	11.5	2.6	0.30
A	1.5	20	9.8	1.72	17.6	2.9	0.51
L	1.0	24	4.0	0.91	22.7	1.8	0.41
D	1.5	26	6.0	0.85	14.2	1.8	0.26
C	1.5	33	5.6	0.84	15.0	1.7	0.26
Average Fired					16.8	2.2 ± 0.2[e]	0.37
				Non-Fired Samples			
I	1.5	7	6.1	0.80	13.0	1.8	0.23
F	1.5	22	4.0	1.78	44.5	1.2	0.53
J	1.5	24	5.0	0.51	10.1	1.5	0.49
G	1.5	30	8.1	1.68	20.7	2.4	0.49
H	1.5	40	5.3	0.77	14.5	1.6	0.23
Average Non-Fired					20.6	1.7 ± 0.2[e]	0.33
Average Fired minus Non-Fired Samples						0.5 ± 0.3[f]	0.04
				Exhaust Samples			
K	60		12.3	1.57	12.8	0.042	0.0054
M	20		3.4	0.91	26.7	0.035	0.0093
Average Exhaust					19.8	0.039 ± 0.004[e]	0.0073
N Filter Blank[d]		----		0.61 ± 0.042[e]	----	-----	-----

a - CAD denotes blowdown angle, θ_{bd}, in crankangle degrees after top dead center
b - All masses are for particles smaller than 1.2-um diameter
c - Mass extract - average filter blank mass
d - Average of three
e - Standard deviation of the mean
f - Estimated rms error

combustion-generated particles, i.e., the difference between the fired and non-fired samples, is much larger than the amount of particulate matter in the exhaust. The average combustion-generated particle concentration is 0.5 ± 0.3 $g\ m^{-3}$, while the average concentration in the exhaust is 0.039 ± 0.004 $g\ m^{-3}$, a factor of more than 12 lower. Thus, although there is considerable scatter, these results suggest significant oxidation of particulate matter formed during the expansion and exhaust processes.

Considerable scatter is present in the measured extractable mass concentrations. Several factors may contribute to this scatter including the relatively small masses measured and possible fuel and lube oil contamination of the blowdown samples. This contamination problem makes it difficult to interpret the extractable mass measurements. However, it does not adversely influence PAC determinations because there are relatively low concentrations of PACs in the fuel and lube oil. This is discussed further below.

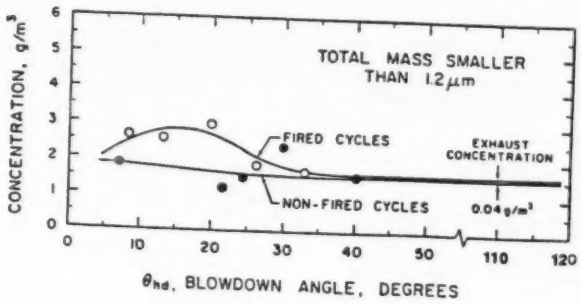

Figure 4 - Total mass concentrations of particles smaller than 1.2-μm diameter as a function of blowdown angle.

Table 4 shows the concentrations, expressed as parts per million by mass in the total sub-1.2 μm diameter particulate matter collected, of the PACs measured in the cylinder and exhaust samples. These concentrations will, to a certain extent, be influenced by chemical reactions and gas-to-particle mass transfer during blowdown and sampling. These influences will be initially ignored. Then their possible impacts on the results will be examined.

Considerable variability is apparent in the results shown in Table 4, but a general pattern exists. This pattern can be more easily seen if the average concentrations for fired, non-fired, and exhaust samples are compared. These comparisons are made in the upper part of Table 5. The 1-nitropyrene concentrations in the exhaust particulate matter are much

Table 4 - PAC Analysis of Filter Samples

Sample	CAD[a]	1-NP[b,c]	PY[b]	B(a)p[b]	B(k)F[b]	FL[b]
		Concentration, Parts Per Million by Mass in Collected Particulate Matter				
			Fired Samples			
B	8	0.64	111	85	30	97
E	13	0.23	74	87	30	52
A	20	0.59	126	115	42	87
L	24	0.20	72	202	64	11
D	26	0.28	60	103	34	142
C	33	0.48	64	92	30	152
			Non-Fired Samples			
I	7	0.16	34	53	16	6
F	22	1.03	105	73	34	41
J	24	0.14	54	41	12	27
G	30	0.68	118	185	60	81
H	40	0.26	77	56	17	31
			Exhaust Samples			
K		18.70	121	46	19	103
M		17.00	222	50	22	181

a - CAD denotes blowdown angle, θ_{hd}, in crankangle degrees after top dead center

b - 1-NP denotes 1-nitropyrene, $C_{16}H_9NO_2$
PY denotes pyrene, $C_{16}H_{10}$
B(a)P denotes benz(a)pyrene, $C_{20}H_{20}$
B(k)F denotes benz(k)fluoranthane, $C_{20}H_{12}$
FL denotes fluoranthene, $C_{16}H_{10}$

c - The 1-NP levels for all fired and non-fired samples were very low accuracy; ± 25%.

Table 5 - Mean PAC Concentrations in Cylinder and Exhaust Samples

Type	1-NP	Pyrene	B(a)P	B(k)F	Fluoranthene
	Mean Concentrations, (Standard Deviation of Mean) in parts per million by mass in particulate matter				
Fired	0.40 (0.08)	85 (11)	114 (18)	38 (5)	90 (22)
Non-Fired	0.45 (0.17)	78 (16)	82 (26)	28 (9)	37 (12)
Exhaust	18.0 (1.0)	172 (51)	48 (2)	21 (2)	142 (39)
	Mean Concentration, (Standard Deviation of Mean) in micrograms per standard cubic meter				
Fired	0.94 (0.24)	199 (44)	248 (34)	84 (12)	196 (40)
Non-Fired	0.76 (0.29)	135 (39)	156 (72)	52 (23)	69 (32)
Combustion	0.19 (0.38)	64 (59)	92 (79)	32 (26)	127 (51)
Exhaust	0.69 (0.10)	6.4 (1.4)	1.8 (0.2)	0.78 (0.02)	5.3 (1.0)
Exhaust / Combustion	3.6	0.10	0.020	0.022	0.042

higher, by a factor of more than 40, than concentrations in the cylinder. Pyrene and fluoranthene concentrations are also higher, but only by a factor of about 2. The other PAHs are present in lower concentrations in the exhaust particulate matter than in the cylinder.

The fuel and lube oil were also analyzed for PAH. Only pyrene and fluoranthene were detected and only in the fuel. Fuel pyrene and fluoranthene were 14,000 and 10,300 μg/L (PPB), respectively. Detection limits for the PAHs in the fuel and lube oil were estimated to be less than 100 PPB under the analytical conditions employed. The observed values are in line with previous analyses of similar fuels. For example, the Department of Energy National Reference #2 Diesel fuel (Phillips lot C345) and fluoranthene, pyrene and B(a)P values of 8,900, 13,000, and 110 PPB respectively (16).

While some of the PAHs observed in the exhaust and cylinder samples may come from the fuel, combustion synthesis is likely also an important source. Yergey, et al., (17) found significant levels of PAHs and 1-nitropyrene in the exhaust particulate extracts of a single cylinder diesel engine operating on a fuel of pure isooctane-tetradecane.

Perhaps more meaningful than PAC concentrations in the collected particulate matter are the corresponding concentrations in the cylinder or exhaust gases. These concentrations have been determined by multiplying the particle mass per standard cubic meter by the PAC concentration in the particles. The results of these calculations are summarized in the lower part of Table 5. Here, a somewhat different but equally interesting picture emerges. The mean concentration of 1-nitropyrene generated by combustion in the cylinder is $0.19 \pm 0.38\ \mu g\ m^{-3}$ which is not significantly different from zero. On the other hand, the exhaust concentration is $0.69 \pm 0.10\ \mu g\ m^{-3}$, on average nearly four times higher. This suggests that this material is formed between the cylinder and the exhaust sampling station. Formation of 1-nitropyrene during the expansion and exhaust processes has been previously suggested (8,9,18). This is, however, the most direct evidence yet presented of this process.

Turning now to the PAHs, the concentrations of all of these species are much lower in the exhaust than in the combustion chamber. Ratios of exhaust to combustion-chamber concentration vary from 0.02 for B(a)P to

0.10 for pyrene. The lower concentrations present in the exhaust suggest that these materials are formed very early in the combustion process and subsequently decay in the high-temperature environment of the expansion stroke and the exhaust process. On the basis of these ratios, it appears that B(a)P and B(k)F are relatively more reactive during the expansion and exhaust processes than fluoranthene and pyrene. It is interesting to note that the average concentration of B(a)P associated with combustion is 92 $\mu g\ m^{-3}$, compared to 1.8 $\mu g\ m^{-3}$ in the exhaust. On the other hand, pyrene appears to be much less rapidly removed and shows concentrations of 64 and 6.4 $\mu g\ m^{-3}$ in the combustion chamber and in the exhaust, respectively. The exhaust concentrations of B(a)P which are typically reported in the literature are much lower than those for pyrene. Our results suggest that the relative concentrations of B(a)P and pyrene, and probably other PAHs, in exhaust samples are at least as much, and perhaps more, influenced by removal processes than by formation processes.

Before drawing any final conclusions from these results, the influence of chemical reactions and gas-to-particle mass transfer during blowdown, dilution, and sampling must be examined. The samples collected in both blowdown and exhaust-sampling experiments contain PACs which may have been formed and become associated with the particulate matter in a variety of ways during the combustion, blowdown, dilution, and sampling processes. Some nitration and oxidation of PAHs probably occurs during the initial phases of blowdown. However, such reactions should be quickly quenched by cooling and dilution and may be regarded as a slight extension of what would have taken place during normal expansion had it not been interrupted. A similar argument may be made about reactions occurring in the exhaust sampling lines and dilution system.

Much concern has recently been expressed about the possibility of artifactual formation of 1-nitropyrene and other nitrated PAHs during filter sampling (6,8,9). The kinetic model of 1-nitropyrene formation during filter sampling proposed by Schuetzle and Perez (8) has been used to estimate the impact of this process on our results. Exhaust, diluted exhaust, and diluted cylinder sample NO_2 concentrations of 23, 0.10, and 0.068 ppm, respectively were assumed (these are upper limits). The only case where the calculations indicate that more than 1 % of the observed 1-nitropyrene might be formed during sampling is that of sample K. (See Tables 3 and 4.) Here the calculations suggest that the long, 66 min., collection time might lead to the formation of as much as 0.39 ppm. This is still only 2 % of the observed concentration and considerably less than our experimental error. Thus, calculations suggest that sampling should not produce significant quantities of 1-nitropyrene in either blowdown or exhaust sampling experiments. The reason that filter sampling artifacts are not significant in our experiments is that very high dilution ratios are used. Thus chemical reactions associated with particle sampling and collection processes probably do not significantly influence our results.

It is more difficult, however, to determine the influence of changes in the partitioning of PACs between the gas and particle phases which might occur during sampling and collection. Calculations have been done using a model of Langmuir adsorption proposed by Natusch and Tompkins (19). Pyrene was used as a model compound, and adsorption energies from 80 to 100 kJ $g\text{-mole}^{-1}$ were considered. The results of these calculations are summarized in Table 6. The calculations indicate that, in equilibrium, the fraction of the pyrene which is particle-bound ranges from essentially zero in the combustion chamber at 2000 K to more than 98 % in the diluted cylinder samples. The equilibrium particle-bound fractions calculated in the exhaust at 450 K increase from 3 to 85 % with increasing adsorption energy. In the diluted exhaust, these fractions range from 91 to essentially 100 %. This suggests, especially in the case of the cylinder samples, that if rapid gas-to-particle mass transfer does not occur during the sampling and collection process, a significant quantity of PACs in the gas phase may be lost.

In order to determine the importance of this potential problem, the rate of the gas-to-particle mass transfer process has been estimated. Adsorption time constants have been calculated using expressions developed from the model by Barris (20). Assuming zero activation energy for adsorption and 100 % collision efficiency leads to time constants of 1 and 2 s

Table 6 - Calculated Equilibrium Particle-Bound Fractions

Adsorption Energy (kJ g-mole^{-1})	Cylinder Sample	Diluted Cylinder Sample	Exhaust	Diluted Exhaust Sample
80	0.0	0.98	0.03	0.91
90	0.0	1.00	0.30	1.00
100	0.0	1.00	0.85	1.00

Assumptions: Pyrene is taken as the model compound. Molecular weight, 202. Surface area 91 $^{o}A^{2}$ per molecule. Surface area of particulate matter, 100 m^{2} gm^{-1}. Particle concentration: 0.5 gm m^{-3} in cylinder, 0.04 gm m^{-3} in exhaust. Pyrene concentrations: 100 $\mu g\ m^{-3}$ in cylinder, 10 $\mu g\ m^{-3}$ in exhaust. Temperatures: 2000K in cylinder, 450K in exhaust. Adiabatic dilution with clean air at 300K. Cylinder dilution ratio, 300. Exhaust dilution ratio, 200.

in the diluted blowdown samples, respectively. These time constants are based on kinetic-theory collision frequencies and represent an upper limit on gas-to-particle mass transfer rates. The collection times for the blowdown samples are in the range of 10-15 s, compared to at least 20 minutes for the exhaust samples. Thus it is possible that there is insufficient time during the blowdown sampling and collection process for gas-phase PACs present in the combustion chamber to become associated with the collected particulate matter. This should not be a problem with the exhaust samples because of the much longer collection time.

These considerations suggest that the low concentrations of 1-nitropyrene in the cylinder samples relative to the exhaust samples might result from the loss of gas-phase material which does not have sufficient time to become adsorbed on the particulate phase during sampling. The same argument also could be made about the four PAHs. However, all of these materials were found in much lower concentrations in the exhaust samples than in the cylinder samples. Since the loss of the gas-phase material from the cylinder samples would act in the opposite direction, our results would then tend to underestimate the extent to which these PAHs are removed by oxidation and other reactions during the expansion and exhaust strokes.

The relative concentrations of PACs observed in fired and non-fired samples are also of interest. The concentrations in the non-fired samples are surprisingly high, on average about 60 % as high as those in the fired samples. Since no fuel is injected in the non-fired blowdown experiments, these samples would not be expected to be associated with a significant gas-phase component. Thus, the observed PACs must reflect, for the most part, particle-bound material which is stable enough to remain associated with the particles which collect on the walls of the combustion chamber. The survival of these PACs on the wall particles is somewhat surprising in view of their reactivity and the severe environment of the combustion chamber. Apparently, they are protected within the thermal boundary layer of the wall.

A consequence of the fact that the concentrations of PACs in the fired and non-fired samples are not too different is that combustion-chamber concentrations are calculated from a difference between two relatively large numbers. This leads to considerable uncertainty in the calculated combustion-chamber concentrations. An improved engine system which allows a very short firing time before blowdown is currently being installed. This greatly reduces the quantity of material on the combustion-chamber walls and consequently the amount of material reentrained in a blowdown experiment. This new system should allow much more accurate determinations of combustion-generated materials.

Another limitation of the current work is the fact that we were unable to measure gas-phase PACs. In a blow-down experiment it is necessary to empty the sampling bag quickly to minimize wall interactions. Thus high flowrates through the filter are used and it becomes difficult to design a practical trap for gaseous PACs passing through the filter. We plan to explore the influence of somewhat reduced sampling flowrates upon our results. These reduced flowrates will increase particle residence time, thus making a trap less necessary, and at the same time make it possible to design a simpler trap.

CONCLUSIONS

Comparisons of combustion-chamber and exhaust particle concentrations reveal that significant oxidation of particulate matter occurs between the combustion chamber and the exhaust manifold. The four PAHs measured exhibited similar behavior and showed at least ten-fold concentration reductions taking place between the cylinder and the exhaust manifold.

1-nitropyrene behaved quite differently and showed a four-fold concentration increase between the cylinder and the exhaust. Part of this increase may have been due to more complete adsorption of 1-nitropyrene on the exhaust particle samples than on those from the cylinder. However, most of this increase is probably due to synthesis of 1-nitropyrene during the expansion stroke and/or in the exhaust process.

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